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The origin of the conduction band in table salt

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A long-standing misinterpretation of the origin of the conduction band in sodium chloride is corrected. We show that this band is primarily derived from chlorine states, and not from sodium states as is generally believed. The anion character of the conduction band holds for the other alkali halides as well. The reinterpretation of this band clarifies why the size of the band gap in these insulators does not depend on the alkali metal in a first-order approximation. © *1999 American Association of Physics Teachers.*

I. INTRODUCTION

Table salt, also known as sodium chloride (NaCl), is a well studied material. Since the electronic structure of sodium chloride is quite simple, it serves as a model compound in solid state physics courses for graduate students.

Sodium chloride belongs to the alkali halides. They form crystals with the structural formula RX where R denotes an alkali metal Li, Na, K, Rb, or Cs and X a halogen F, Cl, Br, or I. All alkali halides exhibit very similar electronic and structural properties. We will mainly deal with sodium chloride, but the conclusions are valid for the other alkali halides as well.

The electronic structure of NaCl can be readily deduced from the atomic energy levels of the separate constituents in an intuitive way. Sodium atoms have one $3s$ electron more than an inert gas configuration. The $3p$ level of chlorine atoms is occupied by five electrons, one electron less than an inert gas configuration. In compound formation the $3s$ electron of the Na atom is transferred to the Cl atom. This results in an insulating crystal with a fully occupied valence band, which is formed by hybridized Cl $3p$ states. The conduction band is commonly attributed to empty Na $3s$ states.

The latter is a widespread error. The origin of this misunderstanding goes back more than half a century. In this paper we will show that in sodium chloride the conduction as well as the valence band is primarily derived from chlorine states.

II. HISTORY

The first paper which discusses the wave function character of the conduction band in NaCl was written in 1936 by Slater and Shockley.[1] At that time it was, of course, not possible to perform elaborate electronic structure calculations, but they succeeded in describing the one-electron energy bands derived from empirical spectral terms of the separate ions. In forming a crystal, the energies of the ionic states change due to the Madelung potential and bands broaden due to the interaction between wave functions centered on neighboring ions. Slater and Shockley argued that the lowest unoccupied levels in NaCl were formed by hybridization of states which originally belonged to the continuum of excited levels of a Cl^- ion with Na $3s$ wave functions. It is remarkable that these authors were intuitively aware of the importance of Cl states for the conduction band.

Their idea was, however, not adopted by other authors, though we did not find any reference in which it was explicitly challenged. One of the oldest textbooks which is concerned with the electronic structure of sodium chloride is *The Modern Theory of Solids* by Seitz.[2] He remarked that the electronic charge of the lowest unoccupied level is more or less uniformly distributed between the positive and negative ions. This is due to the free electron character of the conduction band. Seitz, however, explicitly connected this band with the lowest empty level of the metal ion.

The picture of the conduction band being primarily derived from cation s states remained a paradigm in later years. There are many textbooks on this subject. A few more modern ones which support this idea are Refs. 3 and 4.

Even sophisticated theoretical methods to calculate the electronic structure of solids, based, for instance, on Hartree–Fock or density functional theory (a proper discussion of these methods is given in *Quantum Theory of the Solid State* by Callaway[5]), did not correct the misunderstanding of the conduction band in alkali halides. In a recent paper Ching *et al.* report the band structures of almost all the halides, together with a long list of references to other calculations,[6] none of which recognizes that the interpretation of the conduction band as being derived from cation states is incorrect.

III. CALCULATIONS

The band structure of NaCl has been published many times, but we calculate it once more for the purpose of our argument. We use the localized spherical wave (LSW) method,[7] which is especially suited here since its basis functions are directly related to atomic states. For details of the computation we refer to Ref. 8.

The LSW method makes use of the density functional theory within the local density approximation. It is known that this approximation produces gaps between valence and conduction bands which are smaller than the experimental values. This is, however, of no importance for the character of the conduction bands.[9]

We took unoccupied Cl $4s$, Cl $3d$, Na $3s$, and Na $3p$ states into account in the basis set in order to describe the conduction band as well as possible. The band structure along some high-symmetry lines in the Brillouin zone is shown in Fig. 1. It is in perfect agreement with previous calculations.[6] The zero of energy is taken to be the top of the valence band. The valence band is completely occupied and is primarily formed by Cl $3p$ states.

An analysis of the lowest, unoccupied, conduction band by inspection of the wave functions is not straightforward since the wave functions in this band are quite delocalized. A

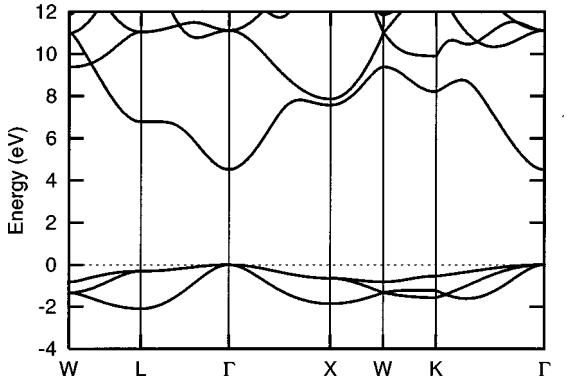

Fig. 1. The band structure of NaCl.

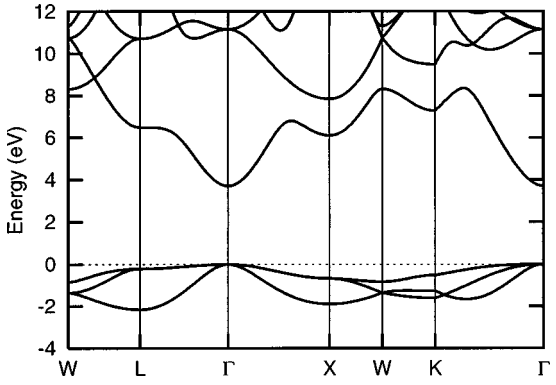

Fig. 3. The band structure of a fcc lattice of Cl^- ions.

good insight is given by a few calculations in which some of the basis functions are excluded from the basis set. Figure 2 shows the band structure of NaCl, calculated without the Cl $4s$ states. The effect of one missing basis function is enormous. The valence bands are unaltered but the conduction band is completely different. For instance, the gap increases and becomes indirect, in contradiction with experiment. This calculation shows that the Cl $4s$ states are, to say the least, very important for the description of the conduction band.

But what about the Na states? We calculate the electronic structure of a fcc lattice of Cl^- ions with the same lattice parameter as NaCl. This can be seen as NaCl with the Na^+ ions taken out altogether. The band structure of the Cl^- lattice is shown in Fig. 3. It shows an astonishing resemblance to the band structure in Fig. 1. The valence bands are identical as expected since these are the Cl $3p$ bands. But also the lowest conduction band and even the bands at higher energies are similar. These bands are formed by Cl $4s$ and Cl $3d$ states. The absence of Na^+ ions causes a different Madelung potential but this merely results in a rigid shift of all the electronic bands.

These calculations reveal the origin of the conduction band. The removal of one single state, the Cl $4s$ state, from the basis set completely destroys the shape of this band. The removal of the Na^+ ion, and of all the basis functions centered on this ion, has no major consequences. This leads to the conclusion that not only the valence bands but also the conduction bands in NaCl are primarily derived from Cl states.

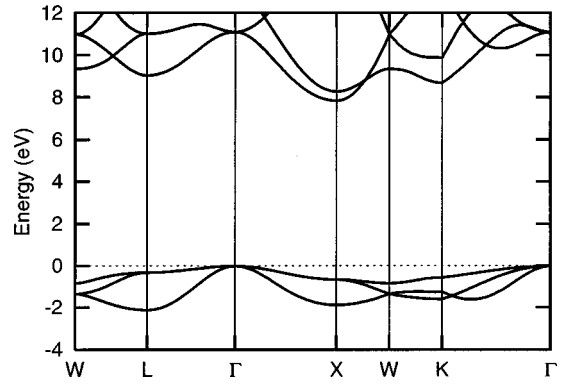

Fig. 2. The band structure of NaCl, without Cl $4s$ states.

IV. BAND GAPS

The character of the lowest unoccupied levels in alkali halides has an interesting consequence for the band gap. In general, the states which are relevant for the size of the band gap of a semiconductor or insulator are, in first approximation, just the highest occupied states and the lowest unoccupied states. Two different situations can be distinguished: (1) The highest occupied states and the lowest unoccupied states are centered on different atoms, and (2) the highest occupied states and the lowest unoccupied states are centered on the same atom.

Examples of the first case are the III–V semiconductors. In these compounds the valence band is primarily derived from anion states, while the conduction band is primarily derived from cation states. The states in these bands interact with each other and therefore the cation states hybridize with anion states and vice versa. This leads to an appreciable anion character of the conduction band and a corresponding cation character of the valence band. This process of hybridization is called covalency. The amount of hybridization influences the size of the band gap and depends, of course, on the cation. This is reflected in Table I, which shows the band gap of a few III–V semiconductors. It is clear that the size of the band gap is strongly dependent on the cation.

The alkali halides, however, behave in a completely different fashion, since both the valence and conduction band are derived from anion states. The anion character of the conduction band is not due to interaction with the valence band and is therefore not related to covalency. Of course, the states in these bands interact with each other as well. But since the cation is not involved in the hybridization of valence band and conduction band states it is expected that the band gap of alkali halides is independent of the cation in first order. This is clearly shown by Table II, which lists the experimental band gap of the alkali chlorides. The cation has almost no influence on the size of the band gap.[12] The inde-

Table I. Experimental band gaps in arsenides.

	Gap (eV)[a]
AlAs	3.1
GaAs	1.5
InAs	0.4

[a]From Ref. 10.

Table II. Experimental band gaps in alkali chlorides.

	Gap (eV)[a]
LiCl	9.4
NaCl	8.5
KCl	8.4
RbCl	8.2
CsCl	8.3

[a]From Ref. 11.

pendence of the band gap of alkali halides on the alkali metal constitutes the experimental evidence for the anion character of the conduction band.

V. CONCLUSIONS

The free electron-like, delocalized, character of the conduction band of NaCl is presumably the main cause of the long-standing misinterpretation of the origin of this band. The question arises whether it is suitable to assign atomic states to a free electron-like band at all. However, if one insists on doing so, the bottom of the conduction band in NaCl—and in the other alkali halides—should be associated with anion *s* wave functions.

This paper shows that simple arguments are not always good arguments. It is very natural, but incorrect, to associate the conduction band in alkali halides with cation states. This fact should be taken into account when the electronic structure of these insulators is presented in introductory classes. It is important that students develop some physical intuition but they should also be aware of the drawbacks of intuitive reasoning.

Furthermore, this paper reveals the value of numerical calculations. The calculation of the band structure of NaCl on its own does not contribute very much to the understanding of the origin of the conduction band. But by turning on and off particular states, which is impossible in the ''real'' physical world, it becomes evident that chlorine states are very important for this band.

Slater and Shockley were right.

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[10]D. J. Arent, ''Band offsets for strained $In_xGa_{1-x}As/Al_yGa_{1-y}As$ heterointerfaces,'' Phys. Rev. B **41** (14), 9843–9849 (1990).

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[12]The weak dependence on the cation is due to the size of the cation which affects the lattice parameter and therefore also the width of bands, and to the slight hybridization of the anion states in the conduction band with cation *s* states at higher energies—and for K, Rb, and Cs with cation *d* states as well.

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People who make their livings in ''soft'' sciences and the arts are not entirely at ease in the company of chemists and physicists and other ''hard'' scientists. In such company, the psychologists and sociologists and the professors of English feel like touch-football enthusiasts who have wandered by mistake into the locker room of the Pittsburgh Steelers. Only true philosophers, not professors of philosophy, are entirely immune to that nasty suspicion that rises in the heart of the ''humanist'' when he hears about recombinant DNA or quarks.

Richard Mitchell, *The Graves of Academe* (Little, Brown and Company, Boston, 1981), p. 43.